

***Ab initio* study of magnetic anisotropy in cobalt doped zinc oxide with electron-filling**

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Based on first-principles calculation, it has been predicted that the magnetic anisotropy energy (MAE) in Co-doped ZnO (Co:ZnO) depends on electron-filling. Results show that the charge neutral Co:ZnO presents a “easy plane” magnetic state. While modifying the total number of electrons, the easy axis rotates from in-plane to out-of-plane. The alternation of the MAE is considered to be the change of the ground state of Co ion, resulting from the relocating of electrons on Co *d*-orbitals with electron-filling.

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Magnetic anisotropy energy (MAE) is a crucial parameter in high density magnetic storage^{1,2}. A large magnitude of MAE will enhance the robustness of one bit to stabilize its magnetic spins. An efficient writing process requires a controllable direction of easy axis, which is determined by the sign of MAE. Co-doped ZnO (Co:ZnO), a possible diluted magnetic semiconductor (DMS) with high Curie temperature (T_c), has been demonstrated to be a strong single ion anisotropy material³. Recently, the dependence of magnetic anisotropy on charge carrier concentration controlled by an external electric field has been observed in DMS⁴. It offers a promising route to apply magnetic recording capability into information processing unit in current semiconductor devices. Therefore, it is highly desirable to understand the relation between MAE and carrier concentration in DMSs.

In this work, we carry out first-principles calculation based on density functional theory (DFT) to obtain MAE in Co:ZnO. Since adding the external electric-field will induce the accumulation of donors (electron/hole)⁵, the variation of carrier concentration is treated as electron-filling in calculations⁶. Then, we investigate the dependence of MAE in Co:ZnO on electron-filling effect.

A $2 \times 2 \times 2$ supercell is created from the wurtzite primitive cell of ZnO with experimental lattice parameters and one Zn atom is substituted by Co ($\text{Co}_{0.0625}\text{Zn}_{0.9375}\text{O}$). With fixed lattice parameters, the internal coordinates are optimized by using Perdew-Burke-Ernzerhof (PBE)⁷ parameterization of generalized gradient approximation (GGA) as implemented in VASP package⁸.

The electronic structure and magnetic properties are calculated after the structure optimization. We employ a corrected-band-gap scheme (CBGS)⁹, enhancing the

TABLE I. The spin moment (M_S) and orbital moment (M_L) (all in μ_B) and MAE (meV) with electron-filling (δN), where δN is the electron number added. The ΔM_L is calculated as $M_L^{[100]} - M_L^{[001]}$.

δN	M_S		M_L		ΔM_L	MAE
	Total	Co	[001]	[100]		
-1.0	3.817	2.959	0.071	0.067	-0.004	0.241
0	2.857	2.611	0.082	0.085	0.003	-0.107
1.0	2.712	2.509	0.111	0.093	-0.018	0.210
2.0	2.449	2.354	0.126	0.096	-0.030	0.319

bandgap of pristine ZnO to 2.8 eV. Besides, the Hubbard U (2 eV) is applied to Co *d*-orbital⁶. The cut-off energy of plane wave is 500 eV. For the integration in Brillouin zone, the tetrahedron method with Blöchl corrections¹⁰ is employed under a $5 \times 5 \times 3$ *k*-mesh. The accuracy of electronic iterations is up to 10^{-6} eV. Then, spin-orbit coupling (SOC) is performed in non-self-consistent calculations based on the wavefunctions and charge distribution from self-consistent calculations without SOC. The MAE is estimated as $\Delta E = E_{[100]} - E_{[001]}$, where $E_{[100]}$ and $E_{[001]}$ are the total energy in [100] and [001] magnetization directions, respectively. Finally, the calculations above are repeated by adding extra electrons (δN) from -1.0 to 2.0 *e* with respect to the initial value.

In Table I, we summarize the results of MAE, spin moment (M_S) and orbital moment (M_L) with electron-filling. Both of the total M_S and the M_S on Co drop monotonously when increasing the number of electrons (Fig. 1). The MAE of charge neutral Co:ZnO is negative, implying an “easy plane” magnetic state, which is in accordance with experimental results shown in Ref. 3. However, when increasing and decreasing one or more

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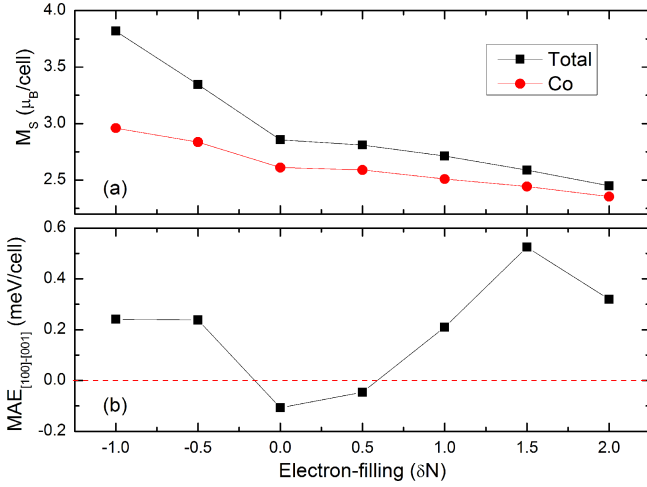


FIG. 1. The dependence of (a) spin magnetic moment and (b) MAE on electron-filling. The positive MAE indicates that the easy axis parallels to the anatase c axis.

electrons, the sign of MAE alters, yielding the direction spin preferred switches from in-plane to out-of-plane. Meanwhile, the magnitude enlarges to more than 0.2 meV, even up to 0.319 meV for $\delta N = 2$. Besides, it should be noted that the M_L in the direction of preferential spin axis is larger than that in another, as given by Bruno's model¹¹. To interpret the variation of MAE with electron-filling, the electronic structure for different electron number is first checked. The density of states are calculated and projected to Co d -orbital for $\delta N = 1, 0$ and 1. For the neutral Co:ZnO [Fig. 2(b)], the gap of pristine ZnO is preserved. The impurity bands, formed by the hybridization between the levels of the host Zn vacancy (oxygen dangling bonds) and Co d -orbital, lie in the bandgap. The Co d -orbital in majority spin, which is just above the valence band maximum (VBM) of the ZnO host, is completely occupied. The topmost occupied state is Co e state in minority spin with 1.5 eV higher than VBM. Additionally, the $e - t_2$ split is about 2.3 eV, and the t_2 state in minority is pushed into conduction band (CB). The system is insulator. Our calculation confirms the electronic configuration of Co^{2+} , d^7 , with a high spin state in neutral Co:ZnO, which is in agreement with previous work⁶.

When decreasing one electron ($\delta N = -1$) [Fig. 2(a)], the initial double degenerated and fully occupied e state of Co in minority spin splits into two bands, one strongly hybrids with valence band of ZnO (O p -orbital) and the other is empty, just locating above the Fermi level. For $\delta N = 1$ [Fig. 2(c)], doping with one electron, the empty t_2 state in minority spin is partially filled. The system becomes metallic. Compared to the neutral system, the electrons relocate in the d -orbital of Co in minority spin when $\delta N = -1$ and 1, which finally results in the change of the ground state of Co ion.

As proposed by van Vleck¹², the MAE is induced by the relativistic SOC interaction. Specifically, for 3d tran-

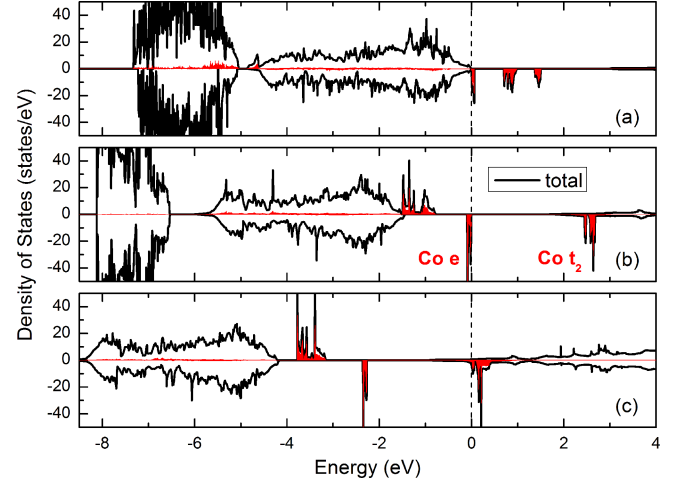


FIG. 2. The density of states with CBGS and $U_{\text{Co}-d}$, (a) $\delta N = -1$, (b) $\delta N = 0$ and (c) $\delta N = 1$. The Co d -orbitals are filled in red color. The vertical dash line refers to the Fermi level.

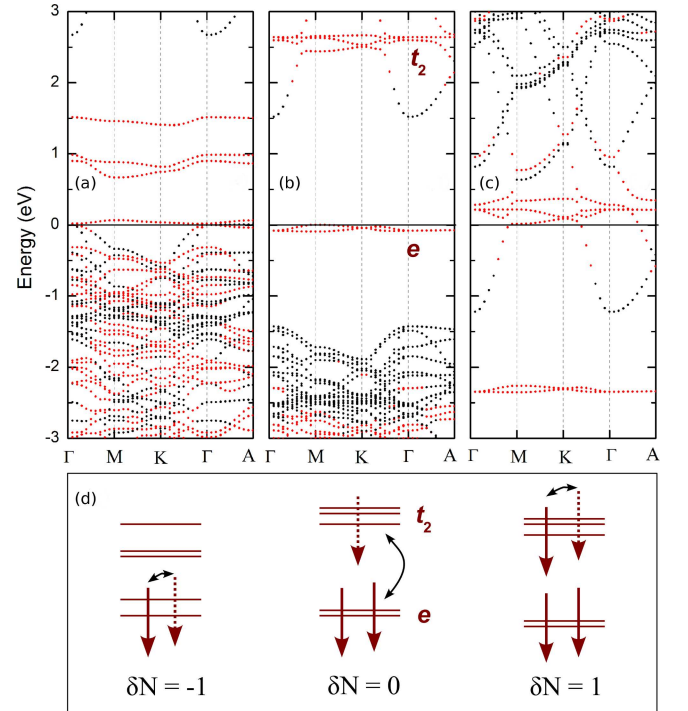


FIG. 3. Bandstructure of minority spin along the high symmetric line in Brillouin zone, (a) $\delta N = -1$, (b) $\delta N = 0$ and (c) $\delta N = 1$. The red color of the point refers to the state with contribution from Co d -orbital more than 2%. The horizontal line at 0 eV is the Fermi level. (d) Schematic diagram (minority spin configuration) of the perturbation determining MAE in Co:ZnO with electron-filling. The MAE for $\delta N = 0$ is decided by the perturbation between the e level and t_2 level. However, that perturbation for $\delta N = -1$ and 1 exists within e and t_2 manifold, respectively.

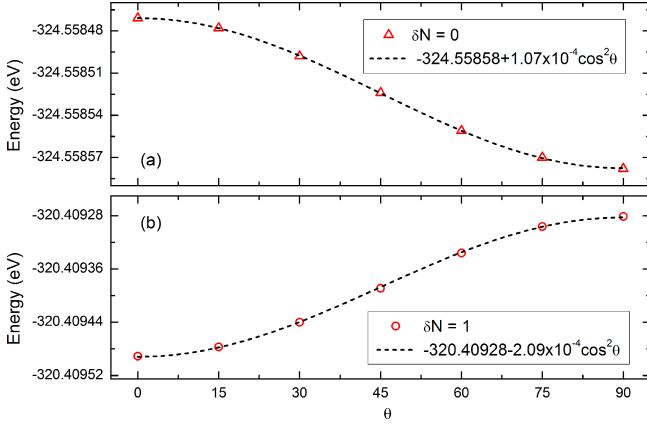


FIG. 4. The dependence of the total energy on the angle (θ) between magnetization direction and the wurtzite c axis, (a) $\delta N = 0$ and (b) $\delta N = 1$.

sition metal elements, the interaction is weaker than the crystal-field split. Therefore, according to the sing-ion anisotropy theory¹³, MAE can be estimated by the second-order perturbation between the ground state and excited states of magnetic ion. Since the Co ion exists as a high spin state in Co:ZnO (Fig. 2), which implies the exchange split is larger than crystal-field effect, and the d -orbital in majority spin is fully occupied, the variation of ground state of Co ion under electron-filling originates from the electron relocating in minority spin.

To describe this physical scenario straightforwardly, we calculate the bandstructure of minority spin for different δN and at the same time mark the state with contribution from Co d -orbital more than 2%, as presented in Fig. 3. For $\delta N = 0$ [Fig. 3(b)], the almost two-fold degenerated e level in ground state is completely occupied, while the t_2 level in conduction band is empty. Therefore, the excited states associate with electrons hopping from the e level and t_2 level, i.e., the MAE for charge neutral Co:ZnO is determined by the perturbation between e level and t_2 level. However, as shown in Fig. 3(a) and (b), this perturbation for $\delta N = -1$ and 1 exists within e and t_2 manifold, respectively. We conclude that the change of the perturbation process [Fig. 3(d)] finally results in the reorientation of easy axis with respect to $\delta N = 0$.

Further, we calculate the total energy as a function of the angle (θ) between the magnetization direction and the wurtzite c axis. Obviously, as shown in Fig. 4, we predict an easy-plane and easy-axis magnetic anisotropic state for $\delta N = 0$ and 1, respectively. Moreover, the trend

of the data implies that the contribution to MAE mainly comes from the second-order uniaxial anisotropy. By fitting the total energy to $C_0 + C_1 \cos^2 \theta$ curve, the standard error for the two coefficients, C_0 and C_1 , up to 10^{-6} supports the former speculation.

In conclusion, first-principles calculations are carried out to investigate the relationship between MAE and carrier concentration in Co:ZnO. Results show that Co:ZnO in neutral possesses an “easy plane” magnetic state. While modifying the total number of electrons by one or more, the system alters the sign of MAE, switching into “easy axis” magnetic state. The electronic configurations on Co ion with electron-filling are checked. We conclude that, due to the electron relocating on Co d -orbital, the perturbation between the ground state and excited states for different total number of electrons has changed, finally reorienting the direction of spin axis. Further, we investigate the dependence of total energy on the magnetization direction. By fitting the data, a second-order uniaxial anisotropy has been found in Co:ZnO.

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